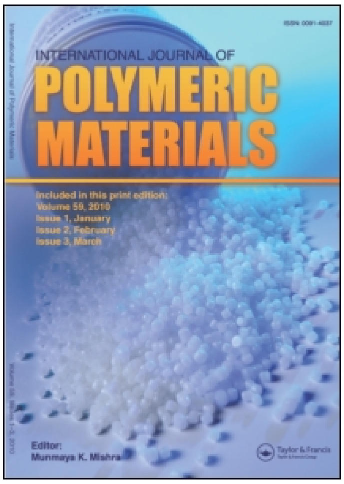

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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Online publication date: 09 November 2010

To cite this Article Parvaiz, M. Rahail , Mahanwar, P. A. , Mohanty, Smita and Nayak, Sanjay K.(2011) 'Fabrication of High Performance Fly Ash/Mica/Poly(ether-ether-ketone) Hybrid Composites', International Journal of Polymeric Materials, 60: 1, 75 — 88

To link to this Article: DOI: 10.1080/00914037.2010.504161

URL: http://dx.doi.org/10.1080/00914037.2010.504161

International Journal of Polymeric Materials, 60:75–88, 2011

ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914037.2010.504161

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This paper deals with the preparation and characterization of poly(ether-ether-ketone) (PEEK) fly ash mica hybrid composites containing filler 5:15, 10:10 and 15:5 fly ash mica combinations loading. The performances and properties of the resulting 20 wt% loading of fly ash mica/PEEK hybrid composites were examined. The resulting hybrid composites of 20 wt% fly ash and mica with varying combinations exhibit the optimum improvement of mechanical properties and dielectric strength. MDSC showed the decrease in the crystallization temperature (Tc) with varying combinations of fly ash and mica. The morphology of fly ash/mica/PEEK hybrid composites was studied by SEM.

Keywords electrical, hybrid composites, mechanical properties, polymer matrix composites, thermal

INTRODUCTION

The reinforcing effect of mineral filler for polymers was recognized after 1930. In the last three decades, improving the mechanical, electrical, thermal and

Received 11 March 2010; accepted 11 May 2010.
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processing properties of polymers with the addition of filler material has become a very popular research interest. Polymer science and technology seek new routes to improve the performance of filled plastic materials while reducing their costs. The key advantage of working with composite materials is the opportunity to integrate material properties and design and manufacturing techniques so that the end product, a completed structure, is optimized for both performance and from an economic standpoint [1–14].

Polyetheretherketone (PEEK) is a high-performance semicrystalline polymer with outstanding thermal stability, wear resistance, mechanical properties, and excellent resistance to chemicals. It has a high melting temperature (T_m) and glass transition temperature (T_g) and continuous service temperature. It can be processed by conventional methods such as injection molding, extrusion, compression molding and powder-coating techniques. Therefore, PEEK and its composites have been reported for use in aerospace, automotive, structural, high temperature wiring, tribology, and biomedical applications [15–27].

The utilization of fly ash (FA) as an additive component in polymer composites has received increased attention recently, particularly for driven/high volume application. This development has been brought about since the incorporation of fly ash has several advantages: it is the best way of disposing of fly ash, and it decreases the overall cost of composites. Fly ash is a waste material, obtained in huge quantities from thermal power plants as a by-product of the burning of pulverized coal. It is a fine and powdery material. A microscopic view would reveal that the particles are essentially spherical. Fly ash has been used as a spherical filler for the production of lightweight, high-strength concrete [28].

Mica is a plate-like crystalline alumino-silicate and has been widely used as a reinforcing filler in polymeric matrices due to its excellent mechanical, electrical, and thermal properties [29]. The commercial delamination of mica may be characterized as wet or dry according to whether the delamination is carried out in a dry state or water. Wet grinding preserves the natural luster and sheen of mica and is normally characterized by clean cut edges, high aspect ratios, smooth surface, and the ability to disperse easily [30]. The results of many experimental studies have shown that the addition of mica to a thermoplastic matrix improves the mechanical, thermal and dielectric properties. Researchers have reported that the addition of mica to a polymer system results in significant improvement in the tensile strength and modulus. Berlin et al. [31] studied the effect of mica as a filler on polymer systems and found significant improvement in flexural properties. Goyal [32] reported improvement in properties on incorporating filler into plastic.

In this study, PEEK-filled fly ash/mica hybrid composites were prepared by compression molding technique to investigate the effect of the fly ash/mica combination on the mechanical and thermal properties such as T_g, T_c, E', tan δ

and morphology of PEEK fly ash/mica hybrid composites were observed by using scanning electron microscopy.

EXPERIMENTAL

Materials

Matrix material polyetheretherketone (Grade 5300) was obtained from Gharada Chemicals, Ltd., Panoli, Gujarat, India. Fillers fly ash and mica of particle size 44 µm were obtained from the Kuradi Thermal Power Plant, Nagpur, India, and Galaxy Corporation Pvt. Ltd., Mumbai, India, respectively.

Preparation of Hybrid Composites

A mixture of fly ash mica compositions used for the present study is 20 wt% with a varying combination of (0:20, 5:15, 10:10, 15:5 and 20:0). Polyetheretherketone, fly ash and mica were predried at $100 \pm 5°C$ for 8 h. prior to compounding. The fly ash mica (20 wt%) was added to polyetheretherketone. The composites were prepared by using melt mixing in a counter-rotating, twin-screw extruder (RC 9000 Haake, Germany). The temperature profiles in the barrel were 200, 250, 320, 340, and 360°C from feed zoon to die. The screw length to diameter ratio (L/D) was 20:1 and the screw speed was 40 rpm. The extrudates were water-cooled at room temperature, and palletized. The palletized granules of PEEK fly ash/mica composites were predried at $100 \pm 5°C$ for 8 h. Test specimens were prepared from compression molding in a sheet mold of $180 \times 180 \times 3\,mm^3$ using a machine from M/s. Sterling Hydraulic Co. Ltd., Mumbai, India. The temperature of the mold plate was $390 \pm 5°C$ with a cycle of time 15 min, breathing was done after 5 min with an interval of 1 min and then kept at $390 \pm 5°C$ temperature and pressure and cooled to 40°C under continuous hydraulic pressure of $180\,kg/cm^2$. Testing samples were prepared according to ASTM standards.

Characterization of Hybrid Composites

Room temperature tensile properties, including tensile modulus, tensile strength and elongation to break, were determined in accordance with the ASTM D638 taking specimens of dimensions $165 \times 13 \times 3\,mm^3$. The tensile testing was carried out using a Universal Tensile Testing Machine (UTM) LR 50 K from Lloyds Instrument Ltd. (UK) at a cross-head speed of 50 mm/min. Flexural properties were measured using a three-point bending test method according to ASTM D790 and tests were carried out using the same UTM, with rectangular bars of dimension $80 \times 12.7 \times 3\,mm^3$. Tests were conducted at a jaw speed of 0.8 mm/min at room temperature. Charpy impact tests were performed using a 2.7 J pendulum and striking velocity of 3.46 m^2/s on an Avery Denison Impact tester (model 6709), according to ASTM D256. The specimen dimension was $127 \times 12.7 \times 3\,mm^3$. The dialectic strength was measured as per ASTM D149 using Zaran Instruments Ltd. India, with a 3 mm thick composite disc. The effect of the treated fly ash on the thermal behavior of the PEEK resin was evaluated using a modulated differential scanning calorimeter (MDSC). The glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) of polyetheretherketone mica composites were studied using MDSC Q100 (TA, USA). Temperature calibration was performed using indium as a reference ($T_m = 156.60$°C and heat flow = 28.5 J/g). The heating rate of the samples was 20°C/min with sample weight between 7 to 9 mg using a standard aluminum sample pan. The experiments were carried out under nitrogen flow of 50 ml/min over a temperature range of 40–400°C. Dynamic mechanical and thermal analysis (DMTA) was carried out in tension mode using a GABO Qualimeter (Eplexor 150 N, Germany) dynamic mechanical and thermal analyzer at a heating rate of 2°C/min and deformation frequency of 10 Hz. The specimen size was 50–40 mm in length, 5–4 mm in width and 2 mm thickness and were cut from the molded sheet. The DMTA test was carried out from the temperature range 40–250°C under the static load of 50 N and dynamic load of 40 N. Before starting the cycle, the specimen was held for 5 min at 40°C to stabilize the position of the clamped. Scanning electron microscopy (SEM) studies of the fractured surface of the tensile specimen were carried out on a Jeol (6380LA, Japan). The specimen was sputter-coated with gold to increase surface conductivity. The digitized images were recorded.

RESULTS AND DISCUSSION

Mechanical Properties of PEEK/FA/Mica Hybrid Composites

Figure 1 depicts the change in tensile strength with varying fly ash/mica composition. As the fly ash concentration with mica increases, the tensile strength increases up to the 10F10 M (10 wt% fly ash : 10 wt% of mica) at higher fly ash concentration, the tensile strength decreases and remains almost constant at higher concentration of fly ash. The increase in tensile strength indicates improved dispersion and reduced the number of failure initiating stress concentration. There is adhesion between the polymer matrix and filler, if there is no or weak adhesion, and tensile strength decreases as already reported. The variation in tensile strength with varying concentrations of fly ash/mica is presented in Figure 1. The tensile modulus increased

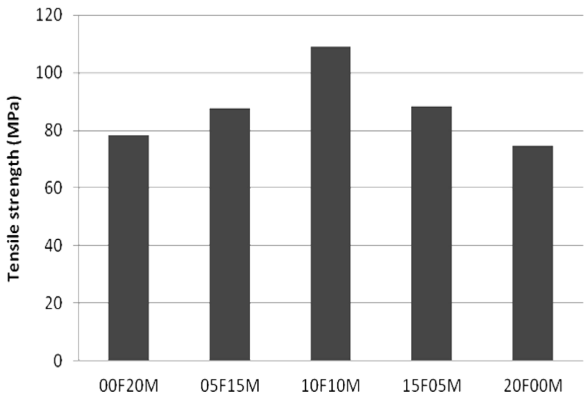


Figure 1: Variation of the tensile strength of different hybrid composites.

with the incorporation of fly ash in combinations of mica hybrid composites. In the constant weight of filler loading (20 wt%) with varying combinations of fly ash/mica shows increased tensile modulus. The PEEK fly ash/mica hybrid composite is shown in Figure 2. It is also observed that the percentage elongation shows the sinusoidal behavior with varying concentrations of fly ash/mica. Percentage elongation decreases at 5F15 M but increases at 10F10 M composition, the decreases at 15F15 M and 20F20 M compositions. At 10F10 M composition, an increase in percentage elongation may be due to the case of orientation of mica along the direction of applied force with the help of small fly ash particles. Especially, the composite of PEEK 10F10 M seems to be the optimum filler composition whose tensile strength, tensile modulus and percentage elongation are highest. The variation in percentage elongation with varying concentrations of fly ash/mica is presented in Figure 3.

Figure 4 shows the variation of flexural modulus with varying fly ash/mica composition. The drastic increase in flexural modulus of PEEK 5F15 M

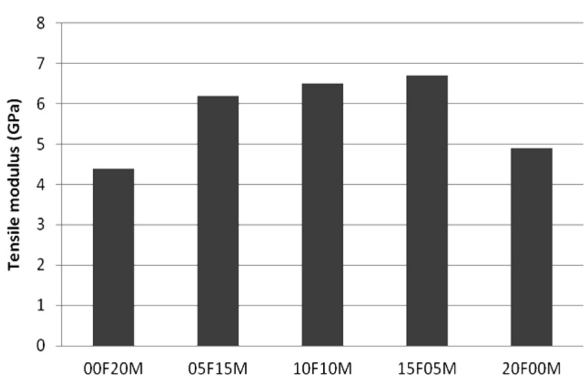


Figure 2: Variation of the tensile modulus of different hybrid composites.

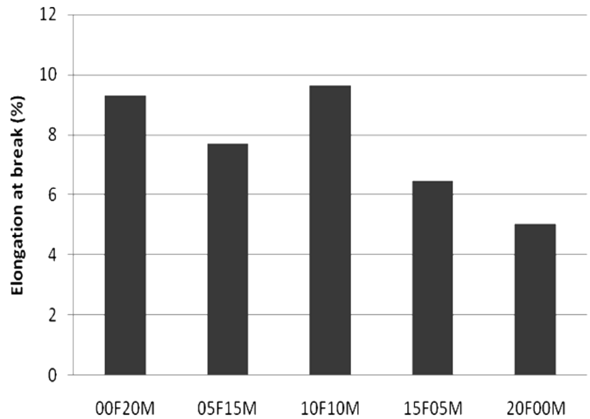


Figure 3: Variation of the elongation at break of different hybrid composites.

composition decreases at high composition of hybrid composites. With the addition of 5 wt% fly ash in 15 wt% mica (5F15 M), the flexural modulus increases 102% compared to PEEK mica composites (0F20 M). The increase in flexural modulus is because the modulus of fly ash is higher than mica filler, therefore the combination of the two fillers increases the flexural modulus of composites. Figure 5 shows the variation in flexural strength with varying composition of PEEK fly ash/mica hybrid composites. The flexural strength slightly increases with the varying composition of fly ash/mica up to 10F10 M, then decreases. The increasing flexural strength is due to mica which forms bridging across the crack initiation point, which is developed by fly ash particle.

It is also observed that the Charpy impact strength decreases with varying combination of fly ash/mica filled composition of PEEK fly ash/mica hybrid

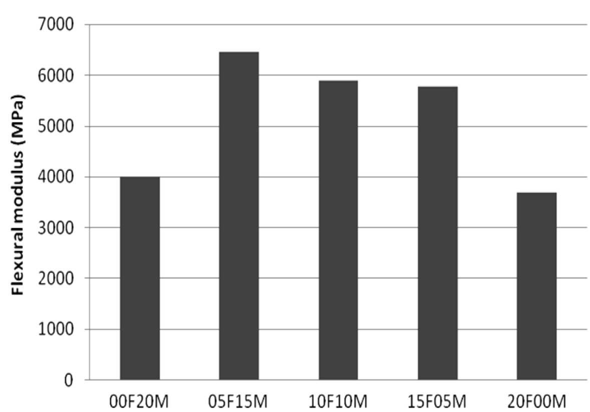


Figure 4: Variation of the flexural strength of different hybrid composites.

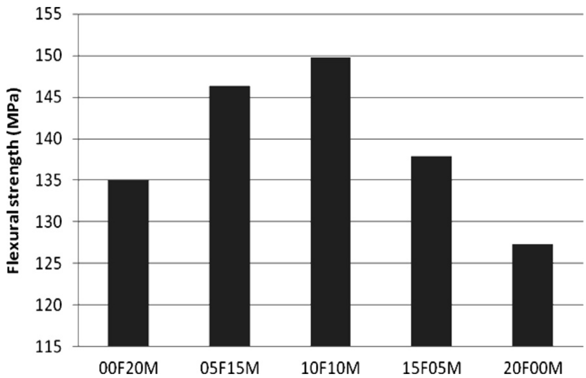


Figure 5: Variation of the flexural strength of different hybrid composites.

composites. The variation of the Charpy impact strength of different hybrid composites is presented in Figure 6.

Electrical Properties of PEEK Fly Ash/Mica Hybrid Composites

Figure 7 depicts the variation in the dielectric strength with varying compositions of fly ash/mica PEEK hybrid composites. The dielectric strength increases with varying composition of fly ash/mica up to the (15F5 M), then drastically decreases at 20F0 M in that only fly ash PEEK composition. The leakage of current in fly ash is less but when platy, filler-like mica improves the dielectric strength. The dielectric strength increases due to the combination of flakes and the spherical-shape filler improved electrical insulation.

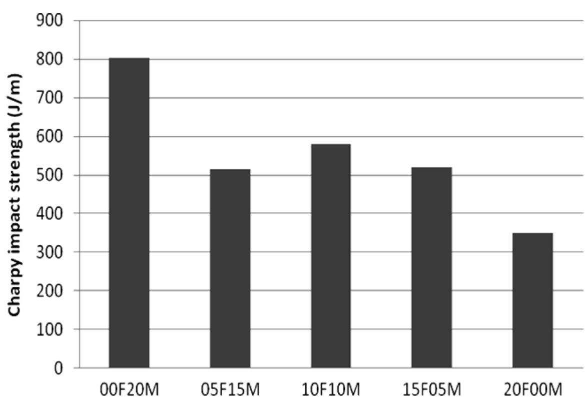


Figure 6: Variation of the Charpy impact strength of different hybrid composites.

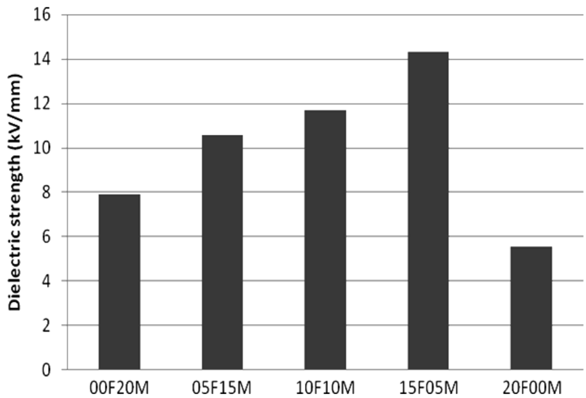


Figure 7: Variation of the dielectric strength of different hybrid composites.

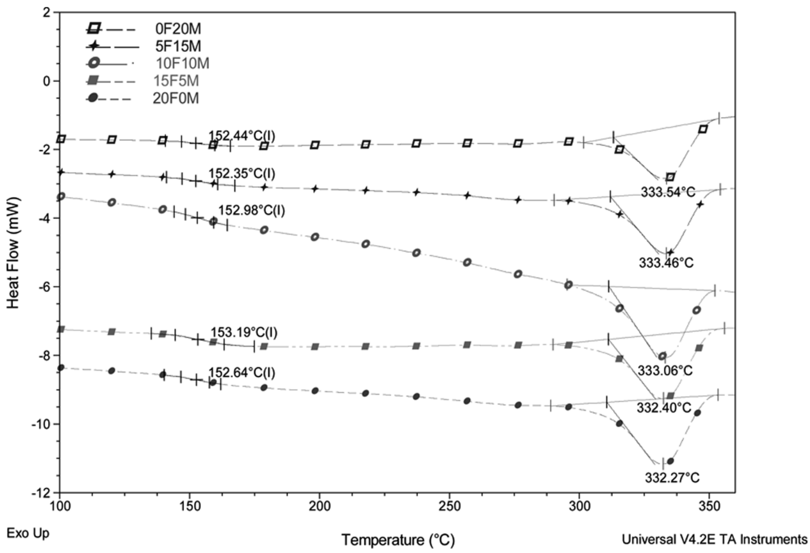
Figure 7 shows the variation in dielectric strength with varying composition of fly ash/mica hybrid composition.

Thermal Properties of PEEK/Fly Ash/Mica Hybrid Composites

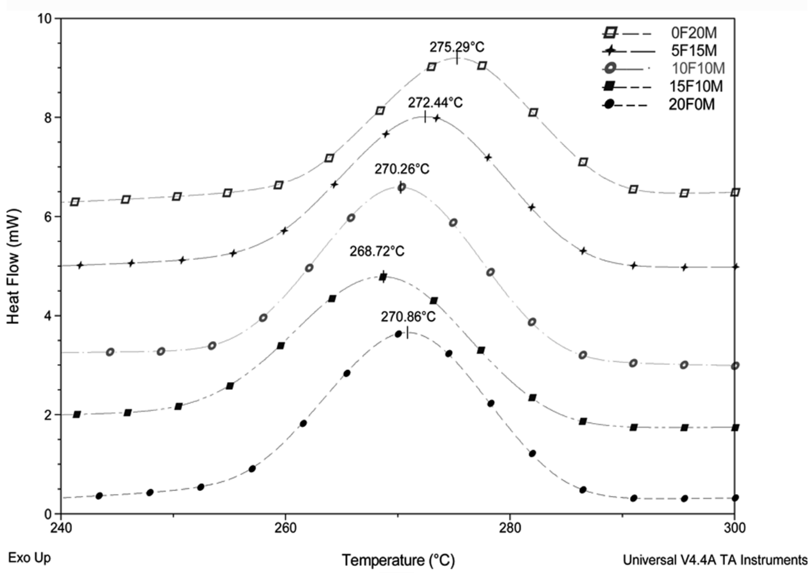
Figure 8(a) depicts the variation of glass transition temperature and melting temperature of PEEK fly ash/mica hybrid composites and PEEK fly ash and PEEK mica composites. There is no significant change in the melting point of both hybrid PEEK fly ash/mica composites in the MDSC diagram. The melting temperature is consistently scattered within $333 + 1°C$ in the typical range of 330–380°C for PEEK resin. Glass transition temperature is also not affected by varying the concentration of fly ash and mica, $152 \pm 1°C$ in the typical range of PEEK resins. The effect of the particle size of fillers and its concentration is not affected to the Tg and Tm of PEEK composites.

Figure 8(b) shows variation in T_c of PEEK fly ash/mica hybrid composites. As for the addition of filler on the crystallization of PEEK, there are several factors involved; some of them are contracting each other, making the net effect abscise at the same time. For example, in terms of heterogeneous nucleation of PEEK on the filler particles interfaces, the crystallization initiation and Tc might increase. However the obstacle effect from the filler particle on PEEK mobility and crystallization would lower the Tc.

The T_c of hybrid composites is decreased as compared to PEEK fly ash and PEEK mica composites as the addition of fly ash 5, 10, 15 wt% and (mica 15, 10, 5 wt%) Tc decreases and shows homogeneous nucleation. The decreases in T_c may be due to the restriction chain mobility of PEEK with different particle size shape filler combinations. The trend of variation of Tc with different



(a)



(b)

Figure 8: MDSC thermograms for (a) second heating curves of T_g and T_m, (b) cooling curves of crystallization temperature T_c of different PEEK fly ash/mica hybrid composites.

hybrid composites, PEEK fly ash, PEEK mica composites are presented in Figure 8(b).

Figure 9(a) depicts the storage modulus vs. temperature with varying composition of PEEK/fly ash/mica hybrid composite. The storage modulus

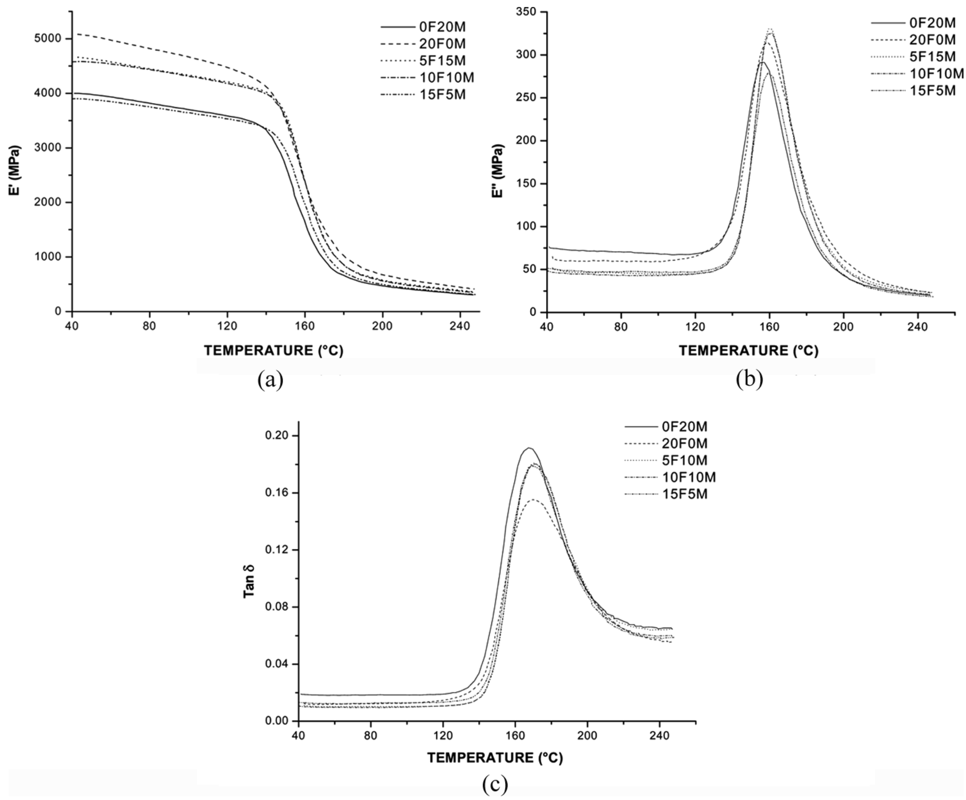


Figure 9: (a) Storage modulus vs. temperature, (b) loss modulus vs. temperature, (c) tan δ vs. temperature of PEEK fly ash/mica hybrid composites.

below the T_g (glassy region) of the PEEK/fly ash/mica hybrid composite maintains plateau and shows no significant difference among the samples. The above T_g (rubbery plateau region), the storage modulus of PEEK/fly ash/mica hybrid composite decreased with increasing temperature. For the rubbery plateau region, the storage modulus of the composite is significantly increased with changing the filler composition, comparing the hybrid composite with PEEK/fly ash and PEEK/mica composite. With the addition of 5 wt% fly ash with 15 wt% mica, the storage modulus drastically increased at 50°C temperature, but as the temperature increased, the storage modulus decreased. The addition of fly ash increased concentration to 10, 15 wt%, with mica 10 and 5 wt%, respectively. Storage modulus decreases but PEEK fly ash composite shows maximum storage modulus compared to hybrid composite. It is observed that from the loss modulus graph that by varying fly ash/mica combination, there is no change in the glass transition temperature. At 50°C the temperature loss modulus decreases by increasing the fly ash concentration in mica than compared with PEEK/mica and PEEK/

fly ash composite. All hybrid composites show lower loss modulus compared to the PEEK/fly ash and PEEK/mica composite. The peak of loss modulus shift to right shows good interaction between filler and matrix. The variation dimensional stability in the composite might be directly reflected in the storage modulus vs. temperature behavior measured in tensile mode. The trend of loss modulus vs. the temperature of different hybrid composites is presented in Figure 9(b).

The damping properties (Tan δ), as the proportion of fly ash increased the Tan δ is decreased compared to PEEK/mica and PEEK fly ash composite at 50°C temperature. The height of Tan (δ) peak corresponds to the polymer chain whose chain mobility is restricted by the fly ash and mica concentration [32]. The Tan (δ) peak height of hybrid composite is in between the PEEK/fly ash and PEEK/mica composite. Figure 9(c) indicates that fly ash shows more chain mobility restriction compared to mica and hybrid shows between. Broadening at tan δ peak observed in hybrid composites shows relaxation strength, even though the integrated area under a tan is more strictly a measure the strength of relaxation.

Morphology of Hybrid Composites

Figure 10 (a-e) depicts the SEM micrographs of PEEK FA mica composites. The pure PEEK had a relatively smooth morphology on the fractured surface upon the addition of fly ash/mica to PEEK, and the morphologies of fractured composites changed dramatically and a very rough surface was observed. It was hard to discern the planar-shaped mica (white circle) from the polymer matrix, but fly ash black circles could be clearly seen from the image. The fly ash and mica are covered with polymer matrix indicating strong interfacial adhesion between filler and PEEK. It is interesting to note that the mica flake oriented in one direction. The fracture surface did not show large voids or micro crack, confirming the assumption of the tensile and flexural properties' behavior that fire-grained particles were located among big particles. This is the reason why partial replacement mica with fly ash as a filler resulted in enhanced mechanical and electrical strength and reduced impact strength.

CONCLUSION

The following conclusions have been drawn from the present study.

The tensile modulus of PEEK fly ash/mica hybrid composites was improved by the incorporation of 20 wt% filler. The optimum strength improvement was observed in the composition of 10F10 M (10 wt% fly ash and 10 wt% mica) filled PEEK hybrid composites. PEEK filled with fly ash

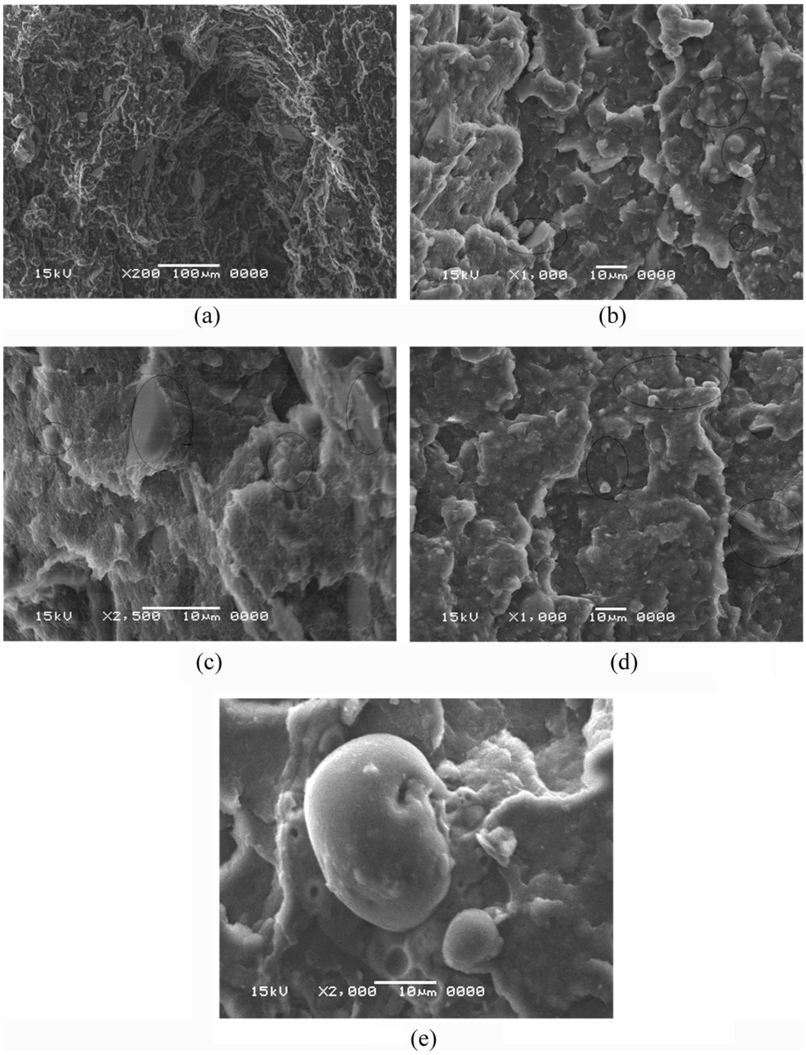


Figure 10: SEM micrograph of fracture surface (a) 0F20M, (b) 5F15M, (c) 10F10M, (d) 15F5M and (e) 20F0M of PEEK fly ash mica hybrid composites.

and mica showed remarkable improvement in flexural strength and modulus. Hybrid reinforcement of filler in polymer shows significant improvement in the dielectric strength of composites. Finally, it can be concluded that the addition of the platelet filler and spherical filler as a hybrid reinforcement in optimum amount and structure can be adjusted so that the composites act as an effective damper at that temperature range of interest with high processing and mechanical performance.

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